portionation yields CH_3CF_3PH and probably more than one other product.

Infrared Spectra

The vapor-phase infrared spectra of ten new CH_3-CF_3P compounds were recorded by means of the Beckman IR7 instrument, calibrated to 1 cm^{-1} although some wide peaks could not be read that accurately. The apparent intensity of each peak or shoulder was calculated as $k = (100/PL) \log I_0/I$ for pressure P and path L both in cm, with I taken literally as per cent transmission; these k values were recorded in parentheses after the respective frequencies (cm^{-1}). Table VII shows the main results, with group-frequency assignments according to experience with many related compounds. However, some assignments remain uncertain: for example, P=O stretching and CH_3 symmetric deformation occur at similar frequencies, and some of the strong peaks in the C—F stretching region may be CF_3 symmetric deformation overtones, greatly enhanced by Fermi resonance. Also, some fundamental modes are missing or unrecognizable. The following notes supplement the tabulated information.

For CH_3CF_3PF, the 808-cm^{-1} band (5 cm^{-1} wide at the peak) could represent coupling of P–F stretching with CH_3 rocking, leaving exact assignments uncertain in this region. Very weak peaks at 2355, 2295, 2255, 1996, 1880, and 1605 cm^{-1} represent overtones and combinations.

For $CH_3OPCH_3CF_3$, combinations and overtones were seen at 2322 (0.2), 2247 (0.2), 2095 (0.1), 1800 (0.2), and probably 577 (0.09) cm^{-1}. For $(CH_3)_3COP$-CH_3CF_3, combinations appeared at 1765 (0.2) and 1637 (0.4) cm^{-1}, and a peak at 489 (0.2) cm^{-1} was not assigned. Similarly, $(CH_3)_3CSPCH_3CF_3$ showed peaks

at 575 (0.8) and 460 (0.14) cm^{-1}, omitted from Table VII for lack of assignment.

The recorded spectrum for $(CH_3CF_3P)_2S$ was relatively simple, not only because band structure was unresolvable, but also because the vapor pressures attainable without decomposition were too low for observation of many weak bands. The simpler phosphine oxides and sulfide could be vaporized at higher temperatures, and showed typical PQR features (central spike and two shoulders). For $(CH_3)_2CF_3PO$, an overtone at 2352 (0.05) and a combination at 1995 (0.15) cm^{-1} were observed.

Mass Spectra

The mass spectra of $(CH_3)_2CF_3PO$, $(CH_3)_3COP$-CH_3CF_3, and CH_3CF_3HPO were recorded in detail, with fluorocarbon calibration of the M-66 instrument. The full record is to be found in the original dissertation.[1]

Miscellaneous Nmr Spectra

Beyond the nmr spectra already listed for seven compounds, the results shown in Table VIII also were recorded. The δ values were measured in ppm, for protons downfield from TMS, for F, upfield from Cl_3CF, and for P, upfield from $P(OCH_3)_3$.

Table VIII. Nmr Comparison of Chloro and Iodo Phosphines

	CH₃CF₃PCl		CH₃CF₃PI	
	δ	J	δ	J
¹H	1.44	10.4 HCP	2.28	11.2 HCP
		0.51 HCPCF		0.36 HCPCF
¹⁹F	112	. . .	144	60.4 FCP
³¹P	63.4	73.6 PCF	118	60.9 PCF

Signs of Phosphorus–Phosphorus Coupling Constants in Coordination Compounds

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Abstract: Using double resonance nmr methods, the signs and magnitudes of the ³¹P–³¹P coupling constant were obtained in 13 complexes of the type *cis*- and *trans*-(OC)₄ML₂ (where M = Cr, Mo, or W), *trans*-(OC)₃FeL₂, and *cis*- and *trans*-PdL₂X₂ (where X = Cl or I) in which L = P(CH₃)₃, P[N(CH₃)₂]₃, or P(OCH₃)₃. The signs and magnitudes of δ(³¹P), δ(¹³C), ³J_PH, ⁵J_PH, ²J_PC, ⁴J_PC, and ¹J_CH and their relationship to the ³¹P–³¹P couplings (²J_PP) are presented and discussed. The *cis* zerovalent group VI complexes have negative ²J_PP values in all cases. The rest of the complexes possess positive ²J_PP values except for chromium. The sign results for the *cis* and *trans* group VI carbonyl complexes are discussed from a Pople–Santry MO point of view. D₄ₕ and C₂ᵥ MO energy level diagrams are presented which appear to be consistent with the signs and trends.

The transfer of nuclear spin information between two phosphorus nuclei bound to a metal atom in a complex such as *trans*-(OC)₄Mo[P(CH₃)₃]₂ is a function of the electron distribution among these atoms and there-

fore such couplings (²J_PP) should reflect some aspects of the nature of phosphorus–metal bonding. Since our original reports[2] on estimating values of ²J_PP from

(1) American Chemical Society Petroleum Research Foundation Fellow.

(2) (a) J. G. Verkade, R. E. McCarley, D. G. Hendricker, and R. W. King, *Inorg. Chem.*, 4, 228 (1965); (b) D. G. Hendricker, R. E. Mc-Carley, R. W. King, and J. G. Verkade, *ibid.*, 5, 639 (1966).

the nmr line shapes of complexes containing two identical ligands, numerous additional constants have become available for a wide variety of ligands in several types of complexes.[3] Before the wide range of magnitudes observed for these spin–spin interactions can become useful in rationalizing their trends in terms of changes in metal–phosphorus bonding, it is of prime importance to know the signs of these $^2J_{PP}$ couplings. The necessity for this information takes on added importance when it is realized that sign inversions of couplings involving ^{31}P nuclei can take place. For instance, $^2J_{PH}$ in $P(OCH_2)_3P$ changes from positive to negative while the opposite occurs for the sign of $^3J_{PP}$ in the series $P(OCH_2)_3P$ to $(OC)_5WP(OCH_2)_3P$ to $OP(OCH_2)_3PO$.[4] Sign inversions for $^3J_{PH}$ and $^2J_{PC}$ are also found from $P(OCH_3)_3$ to $OP(OCH_3)_3$ and for $^1J_{PC}$ and $^2J_{PH}$ from $P(CH_3)_3$ to $P(CH_3)_4^+$ and from $C_6H_5P(CH_3)_2$ to $C_6H_5PH(CH_3)_2^+$.[5]

In a brief communication[6] we showed from double resonance experiments that the signs of $^2J_{PP}$ in cis- and trans-$(OC)_4Mo[P(OCH_3)_3]_2$ were negative and positive, respectively. We now describe these studies in more detail and also report signs and magnitudes of $^2J_{PP}$ and $\delta(^{31}P)$ values for 11 additional complexes of the type cis- and trans-$(OC)_4ML_2$, where M = Cr, Mo, and W, and cis- and trans-PdL_2X_2, where L is $P(OCH_3)_3$, $P(CH_3)_3$, or $P[N(CH_3)_2]_3$ and X = Cl or I. For some of these compounds, the values and signs of the other parameters such as $^1J_{CH}$ and $\delta(^{13}C)$ which determine the appearance of the spectra were also determined. The values and signs of the couplings in $P[N(CH_3)_2]_3$ and $OP[N(CH_3)_2]_3$ were also obtained for comparison with the complexed $P[N(CH_3)_2]_3$. A tentative rationale based on molecular orbital theory is proposed for the marked tendency of the cis group VI carbonyl complexes to possess negative $^2J_{PP}$ values in contrast to the positive values associated with most of the trans isomers. Trends in the other nmr parameters for these and related systems are discussed in terms of electronegativity and bonding considerations.

Experimental Section

The instrumentation employed in the double resonance experiments which yielded the signs of the coupling constants as well as the ^{31}P and ^{13}C chemical shifts is described elsewhere.[4] References to the preparations of the metal complexes are given in the following paper.[3]

Trimethoxymethylphosphonium Tetrafluoroborate. To a suspension of 3.0 g (20 mmol) of trimethyloxonium tetrafluoroborate[7] in 10 ml of methylene chloride was slowly added 2.5 g (20 mmol) of trimethyl phosphite dissolved in 10 ml of methylene chloride. The reaction mixture immediately began to effervesce, indicating the loss of dimethyl ether. Crystals formed upon cooling to −20° which were collected in 50% yield by suction filtration and dried in vacuo. The compound was characterized by its proton nmr spectrum in CD_3CN which indicated a doublet due to the methyl protons at δ 2.14 ppm ($^2J_{PH}$ = 18 Hz) and a doublet due to the methoxy protons, δ 4.10 ppm ($^3J_{PH}$ = 11 Hz) relative to TMS as an internal standard. The integration of the peaks coincided with the expected ratios.

(3) F. Ogilvie, J. M. Jenkins, and J. G. Verkade, *J. Amer. Chem. Soc.*, **92**, 1916 (1970), and references therein.

(4) R. D. Bertrand, D. A. Allison, and J. G. Verkade, *ibid.*, **92**, 71 (1970).

(5) W. McFarlane, *Proc. Roy. Soc., Ser. A*, **306**, 185 (1968); *Chem. Commun.*, 58 (1967).

(6) R. D. Bertrand, F. Ogilvie, and J. G. Verkade, *Chem. Commun.*, 756 (1969).

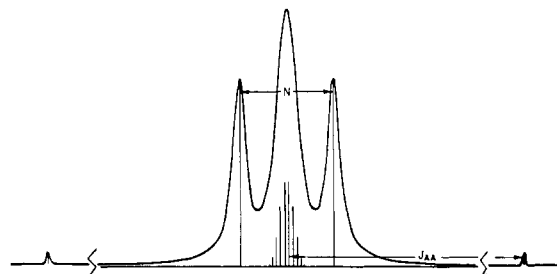(7) H. Meerwein, *Org. Syn.*, **46**, 120 (1966).

Figure 1. Schematic diagram showing the apparent triplet for the X part of an $X_6AA'X'_6$ system arising from overlap of the inner lines when $J_{AA'} \gg L$. The intensity of the first outer pair of lines has been exaggerated.

Results

The parameters which determine the appearance of the X part of the $X_nAA'X'_n$ spectrum are $N = J_{AX} + J_{AX'}$, $L = J_{AX} - J_{AX'}$, and $J_{AA'}$. Harris[8] has derived equations which define the energies and the relative intensities of the X part of the spectrum in terms of these parameters, assuming $J_{XX'} = 0$. The general features of the X spectrum which appear in Figure 1 include a sharp doublet of separation N centered at ν_x as well as $2n$ pairs of lines occurring symmetrically about ν_x. The intensity of this portion of the spectrum is evenly divided between the N doublet and the $2n$ pairs of lines. These $2n$ pairs of lines may be divided into two sets, the so-called "inner" and the "outer" lines. For the typical case in which values of $L/J_{AA'} < 1$, these designations refer to the lines which occur between and outside the members of the N doublet, respectively. Only the first outer pair of lines is represented in Figure 1. Harris also showed[8] that the intensity of the outer lines is quite small compared to that of the inner lines. However, in the event that the first pair of outer lines in the spectrum can be found, it is possible to determine the value of $J_{AA'}$ directly ($^2J_{PP}$ in our application), since the separation between either of these lines and the most intense inner line is $J_{AA'}$.

As the value of $J_{AA'}$ increases for a particular value of N and L, the frequency distribution of the inner and outer lines changes. The separation between the first inner line and the first outer line remains $J_{AA'}$, but the intensity of the outer line decreases as $J_{AA'}$ increases. Hence it becomes experimentally quite difficult to find this line for $J_{AA'} > 100$ Hz at realizable concentrations of the compounds studied. As $J_{AA'}$ increases, the separations of the inner lines becomes smaller until for $J_{AA'} \gg L$ the spectrum appears as an apparent triplet. The distribution of the frequencies and intensities of these inner lines determines the band shape of the portion of the spectrum between the N doublet. Only in rare cases can the fine structure due to the inner lines be resolved, and so only the envelope of these resonances is observed. From line shape considerations, Ogilvie, Jenkins, and Verkade[3] have been able to obtain values of $J_{AA'}$ ($^2J_{PP}$) in coordination complexes by calculating spectra via the equations of Harris[8] and fitting them to the observed band shapes. There are, however, limitations to this method.[3]

In addition to the determination of $J_{AA'}$ from the observation of the first outer pair of lines or from the band shape of the central resonance, $J_{AA'}$ as well as L
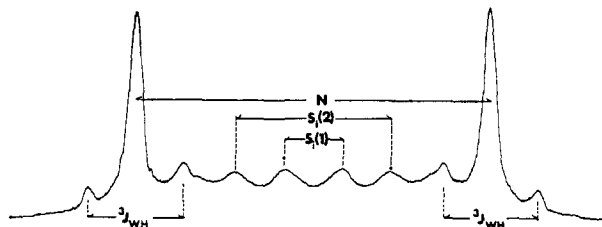
(8) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).

Figure 2. ^{1}H nmr spectrum of cis-$(OC)_4W[P(CH_3)_3]_2$ showing the resolved fine structure. The low-intensity outer bands which were observed are not shown. The meanings and values of the splitting parameters indicated are given in the text.

may be determined from the separations of the first two inner pairs of lines. This is demonstrated for cis-$(OC)_4W[P(CH_3)_3]_2$, the proton spectrum of which is shown in Figure 2. This is the only compound among those studied for which this calculation could be performed since the proton spectra of the remaining compounds did not show the requisite fine structure. Harris has shown that $J_{AA'} = [3S_t(1) + S_t(2)][S_t(1) - S_t(2)]/2[3S_t(1) - S_t(2)]$ and that $L^2 = S_t(1)S_t(2)[S_t(1) + S_t(2)]/[3S_t(1) - S_t(2)]$. Since $S_t(1) = 1.15$ Hz and $S_t(2) = 3.16$ Hz, $^2J_{PP} = 22.9$ Hz and $L = 7.35$ Hz. N is observed directly from the spectrum to be 7.09 Hz. The value of J_{PP} calculated in this manner is in good agreement with that obtained from the separation of the first inner and outer lines (25.0 Hz). It should be pointed out that the calculations of $J_{AA'}$ and L^2 using the above equations are quite subject to errors resulting from imprecision in the determination of the line positions. Using a value for $S_t(1)$ of 1.16 Hz, an increase in this parameter of 0.01 Hz from that observed gives $^2J_{PP} = 20.8$ Hz and $L = 7.11$ Hz if $S_t(2)$ is held at 3.16 Hz. From the definitions of L and N, the value of $^2J_{PH}$ is -7.22 Hz and of $^4J_{PH}$ is $+0.13$ Hz. This compares with a value of -7.34 ± 0.05 Hz for $^2J_{PH}$ and $+0.25 \pm 0.05$ Hz for $^4J_{PH}$ from the curve-fitting procedure employing a value of 25.0 Hz for $^2J_{PP}$.[3]

In addition to the resonance lines arising from the $X_9AA'X'_9$ spectrum of cis-$(OC)_2W[P(CH_3)_3]_2$, there are four additional satellite lines observed due to coupling of the 14% abundant ^{183}W isotope ($I = \frac{1}{2}$) with the protons (Figure 2). The value of $^3J_{WH}$ is determined from the splitting to be 1.93 ± 0.02 Hz. INDOR experiments employing these satellites indicate that $^1J_{WP}$ is 209.8 ± 1 Hz, and of the same sign as $^3J_{WH}$. Because it was not possible to irradiate ^{183}W, we were unable to relate these signs to the sign of N, which is known to be negative (vide infra).

The method by which the value and sign of $^2J_{PP}$ may be determined relative to N in $X_nAA'X'_n$ systems involves double resonance experiments while observing the ^{13}C satellite resonances in the proton spectrum. The experiment necessary for these determinations has been described by Finer and Harris.[9] The ^{31}P resonance for the molecules containing one ^{13}C nucleus appears as two AB patterns because of the two spin states of ^{13}C. Because of the presence of the ^{13}C nucleus in one of the phosphorus-containing moieties, the two phosphorus nuclei are no longer chemically equivalent and so the AB coupling ($^2J_{PP}$ in this case) may be determined from the AB spectrum. Although the intensity of the outer bands in the AB patterns here

(9) E. G. Finer and R. K. Harris, Mol. Phys., 13, 65 (1967).

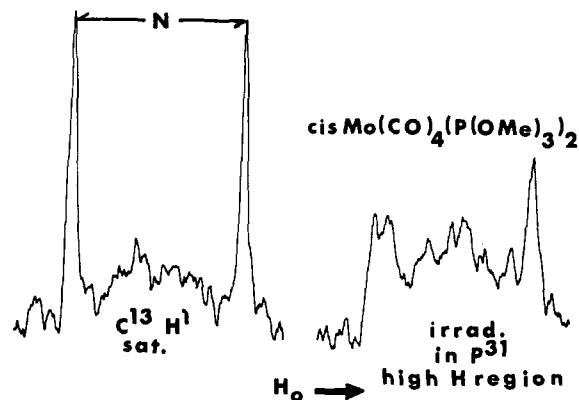Figure 3. Two scans of one of the ^{13}C satellite resonances of cis-$(OC)_4Mo[P(OCH_3)_3]_2$ which demonstrate the determination of the relative signs of N and $^2J_{PP}$. The frequency increases from left to right in both scans. The scan on the left was obtained while irradiating at a frequency 40 Hz greater than the frequency of the center of the central bands of the ^{31}P AB subspectrum. Since the lower frequency member of the N doublet is perturbed, N and $^2J_{PP}$ have opposite signs.

considered are small, a perturbation of one member of the N doublet is observed if sufficient radiofrequency power is applied at the position of any of the weak ^{31}P bands. If for either of the spin states of ^{13}C, the higher frequency weak intensity band is shown to be connected to the higher frequency line of the appropriate ^{13}C satellite, then $^2J_{PP}$ has the same sign as N; otherwise their signs are opposite. It is theoretically possible to show which AB ^{31}P spectrum is connected to which ^{13}C proton satellite, and so determine the relative signs of $^1J_{CH}$ and N_C (which is equal to $J_{PC} + J_{P'C}$).

It was not possible in the case of the trimethyl phosphite complexes to resolve the difference in the frequency of the bands in the phosphorus spectrum due to the two spin states of ^{13}C, since N_C is very small compared to the width of the ^{31}P bands. The ^{31}P bands are broadened by the unresolved proton couplings. Therefore, it was not possible to relate directly the sign of N to the sign of $^1J_{CH}$. However, a complete determination of the signs and magnitudes of the couplings in the liquid complex $(OC)_5Mo[P(OCH_3)_3]$ was performed, and the sign of $^3J_{PH}$ ($=11.6$ Hz) was determined to be positive. It was expected that the sign of N would be positive, since $^3J_{PH}$ is positive in the free ligand ($+10.0$ Hz) and trimethyl phosphate ($+10.5$ Hz)[5] and moreover the observed values are close to the value of 11.6 Hz observed for the trimethyl phosphite complexes. Therefore it is assumed that the sign of $^3J_{PH}$ in the bis(trimethyl phosphite) complexes is positive. Furthermore, it is expected that the contribution to N of the five-bond PH coupling in the bis(trimethyl phosphite) complexes is negligible, since it has been observed for mixed complexes of the type cis- and trans-$(OC)_4$-$MoP(OCH_3)_3P(OCH_2)_3CCH_3$ that no splitting of the main $^3J_{PH}$ doublet due to $^5J_{PH}$ is observed.[10]

Figure 3 shows a comparison of a scan of one of the ^{13}C satellite bands of cis-$(OC)_4Mo[P(OCH_3)_3]_2$ under ordinary circumstances with a scan of this same band when a weak band of one of the AB patterns is irradiated. Irradiating at a frequency of ~ 40.5 Hz less than

(10) F. B. Ogilvie, R. L. Keiter, and G. W. Wulfsberg, Inorg. Chem., 8, 2346 (1969).

Table I. Nmr Parameters for Disubstituted Metal Complexes[a]

Compound	N	N_C[b]	$^1J_{CH}$	$^2J_{PP}$	$\delta(^{31}P)$[c]	$\delta(^{13}C)$[d]
trans-(OC)₄CrL₂	+11.26 ± 0.05[e]		+146.1 ± 0.1	-15.0 ± 0.1[f]	-172.51	
cis-(OC)₄MoL₂	+11.6 ± 0.1[e]	-3.1 ± 0.4	+144.9 ± 0.4	-40.5 ± 0.1[f]	-164.77	-31.29
trans-(OC)₄MoL₂	+11.6 ± 0.1[e]	-1.7 ± 0.4	+144.4 ± 0.4	+162 ± 5[g]	-174.2 ± 0.1	-31.44
cis-PdL₂Cl₂[h]	+12.9 ± 0.2[e]	-3.7 ± 0.2	+148.5 ± 0.2	+79.9 ± 0.2[f]	-96.29	-35.05
trans-(OC)₄CrL₂' [i,j]	-9.84 ± 0.02			-17 ± 5[g]	-178.19	
trans-(OC)₄MoL₂'	+10.2 ± 0.1	+10.6 ± 0.4	+136.1 ± 0.1	+101 ± 1[f]	-154.39	
trans-(OC)₄WL₂'	+10.4 ± 0.1			+81 ± 5[g]	-134.17	
trans-(OC)₄FeL₂'	+9.6 ± 0.1	+5.6 ± 0.4	+135.5 ± 0.1	+65 ± 10[g]	-170.18	
cis-(OC)₄CrL₂'' [i]	-6.9 ± 0.1		+128.7 ± 0.2	-36 ± 1[f]	-6.34	
trans-(OC)₄CrL₂'' [i]	-7.4 ± 0.1			-28.5 ± 1[f]	-21.00	
cis-(OC)₄MoL₂''	-6.30 ± 0.1	+28.5 ± 0.4	+129 ± 1	-29.7 ± 0.1[f]	+17.75	-5.58
cis-(OC)₄WL₂'' [i]	-7.09 ± 0.2			-25.0 ± 0.1	+40.53	
trans-PdL₂L''₂[h]	-7.0 ± 0.1	+37.4 ± 0.4	+130.4 ± 0.1	+572 ± 5[g]	+27.71	-0.25

[a] The spectra were obtained in benzene-d_6, except where indicated. L = P(OCH₃)₃, L' = P[N(CH₃)₂]₃, L'' = P(CH₃)₃. [b] These values were obtained from ¹³C INDOR spectra. [c] ³¹P chemical shifts are in ppm with respect to 85% phosphoric acid and are precise to ±0.02 ppm except where noted. The $\delta(^{31}P)$ values for P(OCH₃)₃ and P(CH₃)₃ are -140 and +62 ppm, respectively (see ref 24), and -122 ppm for P[N(CH₃)₂]₃ (see Table II). [d] ¹³C chemical shifts are in ppm with respect to the ¹³C methyl group of neat glacial acetic acid and are precise to ±0.02 ppm. [e] The sign of this value was assumed to be the same as $^3J_{PH}$ in (OC)₅MoP(OCH₃)₃, since for the disubstituted compound the separation of the resonances due to the two spin states of ¹³C in the ³¹P INDOR spectrum could not be distinguished (see text). [f] Determined from the separation of the first outer pair of lines from the first inner pair of lines in the ¹H spectrum (see text). [g] Determined from the difference in the frequency of the central band and the outer band of the AB spectrum in the ³¹P region as determined by the INDOR technique. [h] Determined on a saturated solution in CDCl₃. [i] Determined on a saturated solution in CS₂. [j] The sign of $^2J_{PP}$ for this compound was related to N by the double resonance techniques described in the text. The sign of N was assumed from the results of the experiments on the other disubstituted complexes of the same ligand.

the frequency of the center of the same AB pattern causes the high-frequency line to be broadened compared to the low-frequency line. The somewhat decreased intensity of the low-frequency line is undoubtedly due to the fact that the center bands of the AB pattern have some intensity at the weak outer bands and so high radiofrequency power is required to cause the observed effect. This result indicates that $^3J_{PP}$ is of opposite sign to N and hence $^3J_{PP}$ is negative. For the complexes of the other ligands that were studied, it was possible to relate N to $^1J_{CH}$, and so $^3J_{PP}$ could be related to $^1J_{CH}$.

For the P[N(CH₃)₂]₃ complexes of Cr and W, the sign of N was assumed positive, as it was found to be positive in the complexes of this ligand with Mo and Fe. Furthermore, the sign of $^3J_{PH}$ was observed to be positive in the free ligand and its oxide; also, as with the trimethyl phosphite complexes, the contribution of $^5J_{PH}$ to N is expected to be negligible since it has been observed that for mixed complexes of the type (OC)₃-Fe[P(OCH₂)₃CCH₃][P(N(CH₃)₂)₃], no splitting of the main $^3J_{PNCH}$ doublet due to $^5J_{PH}$ is observed.[10] For the Cr and W complexes of P(CH₃)₃, N was assumed negative as was the case for the Mo and Pd complexes of this ligand. The results of the nmr studies of the disubstituted transition metal carbonyl complexes in which the signs of $^3J_{PP}$ were determined are given in Table I. The results of the nmr study of the compounds P[N(CH₃)₂]₃, OP[N(CH₃)₂]₃, and (OC)₅Mo[P(OCH₃)₃] are given in Table II. The nmr parameters for [CH₃P(OCH₃)₃]BF₄ were also determined and are presented in Table III. The ³¹P chemical shifts were calculated as previously described.[4] The ¹³C chemical shifts are reported relative to external ¹³CH₃COOH.

Discussion

N, N_C, **and Related Coupling Constants.** As indicated in the Results, the value of N for the trimethyl phosphite complexes is expected to very nearly equal to that of $^3J_{PH}$. The values reported for N and $^3J_{PH}$ in Tables

Table II. Nmr Parameters for P[N(CH₃)₂]₃, OP[N(CH₃)₂]₃, and (OC)₅Mo[P(OCH₃)₃]

Parameter	P[N(CH₃)₂]₃	OP[N(CH₃)₂]₃	(OC)₅Mo-[P(OCH₃)₃]
$^1J_{CH}$	+133.5 ± 0.1[a] +133.6 ± 0.4[b]	+136.2 ± 0.4[b]	+146.8 ± 1[a] +146.2 ± 0.4[b]
$^2J_{PC}$	+19.4 ± 0.4	+2.2 ± 0.4	-2.3 ± 0.4
$^3J_{PH}$	+8.8 ± 0.1	+9.30 ± 0.03	+11.6 ± 0.2
$|^3J_{CH}|$	4.1 ± 0.5	4.1 ± 0.4	
$\delta(^{31}P)$[c]	-121.85	-23.01	-161.22
$\delta(^{13}C)$[d]	-26.94	-16.82	-31.24

[a] Determined from the ¹H spectrum. [b] Determined from the ¹³C INDOR spectrum. [c] ³¹P chemical shifts in ppm are relative to 85% phosphoric acid and are precise to ±0.02 ppm. [d] ¹³C chemical shifts in ppm are relative to the ¹³C methyl carbon of glacial acetic acid and are precise to ±0.02 ppm.

Table III. Nmr Parameters for [CH₃P(OCH₃)₃]BF₄

Parameter	Value[a]
$^1J_{CH}$[b]	+140.9 ± 0.1
$^1J_{CH}$[c]	+153.0 ± 0.1
$^1J_{PC}$	+132.4 ± 0.4
$^2J_{PC}$	-6.8 ± 0.4
$^2J_{PH}$	-17.8 ± 0.1
$^3J_{PH}$	+11.4
$\delta(^{31}P)$	-53.95 ± 0.02
$\delta(^{13}C)$[b]	+14.59 ± 0.02
$\delta(^{13}C)$[c]	-48.47 ± 0.02

[a] Coupling constants are in Hz. ³¹P chemical shifts are relative to external 85% H₃PO₄. ¹³C chemical shifts are relative to the ¹³C methyl carbon of external glacial acetic acid and are given in ppm. [b] The carbon referred to in this parameter is the phosphine carbon. [c] The ¹³C carbon referred to in this parameter is that of the methoxy carbon.

I and II for the complexes of P(OCH₃)₃ compare favorably with the values for P(OCH₃)₃ (+10.0 ± 0.1 Hz) and OP(OCH₃)₃ (+10.5 ± 0.1 Hz)[5] and the value reported for [CH₃P(OCH₃)₃]⁺ (+11.4 Hz). Although the s character in the PO₃ bonds might be expected to change from P(OCH₃)₃ to OP(OCH₃)₃ to [CH₃P-(OCH₃)₃]⁺, the observation of a nearly constant $^3J_{PH}$

value may indicate that a compensating effect operates in the OC and/or CH bond. It is very likely that the stereochemistry of the POCH bond system plays a major role in the $^3J_{PH}$ coupling constant, since in the constrained phosphite molecules $P(OCH_2)_3CCH_3$ and $P(OCH_2)_3P$ $^3J_{PH}$ is 1.8 Hz[3] and 2.5 Hz,[4] respectively, while in $OP(OCH_2)_3CCH_3$ and $OP(OCH_2)_3PO$, it is 7 Hz[11] and 8.3 Hz,[4] respectively. In the transition metal complexes of the constrained phosphites $^3J_{PH}$ possesses intermediate values.[3,4] The relatively unrestricted rotation of the $-OCH_3$ groups in the open-chain compounds probably allows $^3J_{PH}$ to average to a value which is larger than in the analogous bicyclic compounds.

Considering the values and signs of N_C and $^2J_{PC}$ for the trimethyl phosphite complexes, it appears that there is a negligible contribution to N_C in the disubstituted complexes of this ligand from $^4J_{PC}$. Thus N_C for these compounds nearly equals $^2J_{PC}$. The values of N_C reported in Table 1 are between the $+10.0 \pm 0.2$ Hz reported for $P(OCH_3)_3$ and -5.8 ± 0.2 Hz for $OP(OCH_3)_3$,[5] which is slightly higher than the -6.8 ± 0.4 Hz observed for $^2J_{PC}$ in $[CH_3P(OCH_3)_3]^+$ (Table III). We conclude from this observation that as the electron-withdrawing power of the group attached to phosphorus is increased, the two-bond P-O-C coupling becomes more negative. This trend is the same as that observed for the change in the two-bond P-C-H coupling as more electronegative groups are attached to phosphorus.[4]

It is probable that the N values reported for the complexes of $P[N(CH_3)_2]_3$ are essentially $^3J_{PH}$, as was the case for the complexes of $P(OCH_3)_3$, since no splitting of the N doublet due to $^5J_{PH}$ was observed in the ^1H spectrum of mixed ligand complexes in which $P[N(CH_3)_2]_3$ was one of the ligands.[10] The sign determinations for $^3J_{PH}$ reported in this paper are believed to represent the first such investigations involving a three-bond coupling through a nitrogen bound to phosphorus. The positive signs for these three-bond couplings are not unexpected in view of the fact that the same sign is observed for the analogous coupling in phosphites and their derivatives. As with the phosphite complexes, the transition metal complexes of $P[N(CH_3)_2]_3$ possess $^3J_{PH}$ values slightly larger than in the corresponding oxide. McFarlane has determined the $^3J_{PH}$ coupling in $P(C_2H_5)_3$ to be $+13.8 \pm 0.1$ Hz.[5] The values of 10.0 Hz and 8.8 Hz for $^3J_{PH}$ in $P(OCH_3)_3$ and $P[N(CH_3)_2]_3$, respectively, reveal no obvious correlation between this coupling and the electronegativity of the intervening atom attached to phosphorus.

It cannot readily be said that N_C for the complexes of $P[N(CH_3)_2]_3$ does not contain a significant contribution from $^4J_{PC}$. The two values which are reported for this parameter differ by 5 Hz, and no monosubstituted complex of this ligand was studied. However, it is felt that $^4J_{PC}$ is not significant since it was found to be negligible for the trimethyl phosphite complexes. As in the case of trimethyl phosphite and its complexes, the values of N_C are intermediate between the $^2J_{PC}$ values observed in the free ligand ($+19.4$ Hz) and its oxide (2.2 Hz). The trend towards less positive or more negative two-bond couplings with increasing electron-

withdrawing power of the group attached to phosphorus is again observed.

It was also found for $P[N(CH_3)_2]_3$ and its oxide that the ^{13}C INDOR spectrum of these compounds for a given spin state of ^{31}P and ^{13}C was a quartet. The extra splitting is interpreted as arising from the long-range coupling between the ^{13}C and the three protons attached to the other methyl group on the nitrogen atom. The value of this coupling is reported in Table II, but the sign of $^3J_{HC}$ was not determined.

It was shown by Ogilvie, Jenkins, and Verkade[3] from curve fitting techniques that N in the group VI complexes of $P(CH_3)_3$ reported in Table I has at most a contribution of $+0.3$ Hz due to $^4J_{PH}$. The values they reported are $+0.2 \pm 0.2$ Hz for $cis-(OC)_4CrL_2$, $+0.3 \pm 0.2$ Hz for $trans-(OC)_4CrL_2$, $+0.3 \pm 0.2$ Hz for $cis-(OC)_4MoL_2$, and $+0.25 \pm 0.05$ Hz for $cis-(OC)_4WL_2$. It was reported by Goodfellow[12] that $^2J_{PH}$ is 10.1 Hz and that $^4J_{PH}$ is 2.7 Hz (for the $P(CH_3)_3$ moiety) in $trans-PdI_2P(CH_3)_3P(C_2H_5)_3$. Thus, if $^4J_{PH}$ were opposite in sign to $^2J_{PH}$, they would sum to give 7.4 Hz. The value of -7.0 Hz for N in $trans-PdL_2I_2$ thus suggests a $^2J_{PH}$ of ~ -10 Hz and $^4J_{PH} = \sim +3$ Hz. Indeed, using the value for $^2J_{PP}$ for this complex (Table I), values of -10.0 ± 0.2 Hz and $+3.0 \pm 0.2$ Hz, respectively, were obtained for these couplings by a band-shape analysis.[3]

It is noted again that by increasing the electron-withdrawing power of the groups attached to phosphorus in the order metal < chalcogen, the $^2J_{PH}$ coupling constant decreases from $+2.7$ Hz in $P(CH_3)_3$[5] to ~ -7 Hz in the neutral group VI complexes, to -10.0 Hz in the positively charged $trans-PdI_2L_2$, and finally to -13.0 Hz in $SP(CH_3)_3$ or $SeP(CH_3)_3$. In this regard it should be pointed out that when phosphorus is quaternized to $(CH_3)_4P^+$ or $(CH_3O)_3PCH_3^+$, $^2J_{PH}$ becomes -15.4 Hz[5] and -17.8 Hz, respectively. Manatt and coworkers[13] discussed sign data obtained on other phosphine derivatives which also indicated that as the s character in the P-C bonds increases due to increasing electronegativity of the group on phosphorus,[2] $^2J_{PH}$ should become less positive or more negative.

It is noted that even though the two-bond couplings in the neutral trimethyl phosphite and the trimethylphosphine derivatives change sign in contrast to the $P[N(CH_3)_2]_3$ derivatives, the range of values is nearly the same in these three cases (15.8 Hz, 15.7 Hz, and 17.2 Hz, respectively). This is surprising considering the fact that the magnetogyric ratio of ^{13}C is about one-fourth that of ^1H, and, all else being equal, the range of the two-bond P-C couplings might have been expected to be about one-fourth of that of the two-bond P-H couplings. This phenomenon does not seem to be dependent upon the fact that carbon intervenes between the proton instead of oxygen or nitrogen, for it has been reported that $^2J_{PC}$ in $(C_2H_5)_4P^+$ is -4.3 compared to the $^2J_{PC}$ value of $+14.1$ in $P(C_2H_5)_3$[5] giving a range of 18.4 Hz (which corresponds to the 16.8 Hz difference between $^2J_{PC}$ for $P(OCH_3)$ and $[CH_3P(OCH_3)_3]^+$). It is therefore expected that $^2J_{PC}$ in $OP(C_2H_5)_3$ is somewhat higher than -4.3 Hz. This unexpected sensitivity of $^2J_{PC}$ to substitution at phosphorus requires further study.

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It is difficult to assess the contribution of $^3J_{PC}$ to N_C in the $P(CH_3)_3$ complexes, since the observed range of values for $^1J_{PC}$ is quite large (-13.6 Hz for $P(CH_3)_3$ to $+56$ Hz for $(CH_3)_3PS)^5$ and the values observed for N_C in these complexes are intermediate between these extremes, as is expected. It is noted that $^3J_{PC}$ is $+4.9$ Hz and $+6.8$ Hz for $P(OCH_2CH_3)_3$ and $OP(OCH_2CH_3)_3,^5$ respectively, so that $^3J_{PC}$ in the complexes could be of similar magnitude.

It is interesting that $^1J_{PC}$ in $[CH_3P(OCH_3)_3]^+$ is $+132.4$ Hz compared to $+55.5$ Hz in $P(CH_3)_4^+$. It might be argued that this is a result of an increase in the s character of the P–C link in the former compound for two reasons. First, the replacement of the three methyl groups with three methoxy groups would be expected[14] to increase the s character in the phosphorus orbital involved in bonding to carbon. The Pople–Santry[15] molecular orbital treatment for the contact interaction results in the following proportionality for the coupling constant where $(S_i|\delta(r_i)|S_i)$ is the square of the electron density at nucleus i

$$J_{ii'} \propto -(S_i|\delta(r_i)|S_i)(S_{i'}|\delta(r_{i'})|S_{i'})\sum_k^{occ} \sum_l^{unocc}(E_k -$$

$$E_l)^{-1}C_{ki}C_{li}C_{ki'}C_{li'}$$

where $(E_k - E_l)$ is the energy difference between occupied and unoccupied MO's that involve s electron density at the coupling nuclei, and the C's are the coefficients of the atomic orbitals in the LCAO approximation. In this treatment, the increase in s character represents an increase in the value of the C's for the contribution of the phosphorus atom to a σ MO, which results in an increase in the contribution of a positive term in the contact interaction. Furthermore, it might be expected that the phosphine carbon and the phosphorus in $[CH_3P(OCH_3)_3]^+$ support more positive charge than do any one of the methyl groups or the phosphorus in $[(CH_3)_4P]^+$. This would in general lead to a greater value for $(S_{3sP}|\delta(r_0)|S_{3sP})(S_{2sC}|\cdot\delta(r_0)|S_{2sC})$ in the above equation, thus leading to an increase in the positive PC coupling in $[CH_3P(OCH_3)_3]^+$ compared to $[(CH_3)_4P]^+$. This reasoning is supported by considering the values of $^1J_{CH}$ in these compounds which are 142.9 Hz for the phosphine methyl carbon in $[CH_3P(OCH_3)_3]^+$ and 132.5 Hz in $[(CH_3)_4P]^+$. Although it might be argued that this change is due to the increased effective electronegativity of the phosphorus, it is felt that the increase in the positive charge which the phosphine methyl group in $[CH_3P(OCH_3)_3]^+$ must support is largely the cause of the increase of s electron density at carbon for the following reasons. It is found experimentally that increasing the electronegativity of groups attached to the atom bound to a methyl carbon has a very much smaller effect[16] on the CH coupling constant than is observed here (compare $^1J_{CH}$ for CH_3COOH of 130 Hz with CH_3CHO of 127 Hz, or, CH_3CN of 136 Hz with CH_3CCl_3 of 134 Hz). The changes in the energy levels of the σ molecular orbitals which would be brought about by this redistribution of positive charge are difficult to assess. It might be ex-

pected that both the phosphorus 3s and carbon 2s orbitals would be lowered in energy as these atoms support more positive charge and hence the change in the $\sigma \rightarrow \sigma^*$ excitation energy may or may not be changed.

$^1J_{CH}$ **Values.** The $^1J_{CH}$ values for the various ligands and their complexes seem to follow the expected trend. $^1J_{CH}$ should increase as the substituent attached to carbon increases its electronegativity in the order $P < N < O$ since increasing the electronegativity of a carbon substituent is expected to result in increased s character for the CH bonds. This observation has a theoretical basis in valence bond theory[17,18] and numerous empirical correlations are in agreement with this observation.[19–22] The idea that hybridization is solely responsible for the observed trends has been criticized, however, by Grant and Litchman,[23] who have included the effective nuclear charge on carbon in considering coupling between directly bonded carbon and hydrogen. Since the coupling is proportional to the third power of this parameter, small changes in the effective nuclear charge will greatly affect $^1J_{CH}$. Increasing the electronegativity of atoms attached to carbon should increase the effective nuclear charge; hence the coupling constant $^1J_{CH}$ should also increase. In the Pople–Santry molecular orbital treatment,[15] increasing the charge on the carbon should tend to increase $^1J_{CH}$. Furthermore, as the s character in the CH bond increases, as reflected by increasing the coefficients (C) in the coupling proportionality above, the positive $^1J_{CH}$ should become more positive.

^{31}P **and** ^{13}C **Chemical Shifts.** It is observed for the zerovalent transition metal complexes that the ^{31}P nucleus becomes more deshielded upon complexation, and the size of this shift for a particular metal is similar to that observed for other complexes of phosphines,[24,25] phosphites,[24,26] and $P[N(CH_3)_2]_3$.[10] In the two Pd(II) complexes, both upfield and downfield shifts are observed as noted earlier for charged complexes.[27]

The changes in the ^{13}C chemical shifts are somewhat erratic. For the complexes of $P(OCH_3)_3$ (Tables I and II), a deshielding of 3.61 ppm is observed in going from the neutral molybdenum complexes to the dipositive palladium complex. The same trend was observed when comparing the ^{13}C chemical shift of $P(OCH_3)_3$ with $OP(OCH_3)_3$, where the electronegative phosphoryl oxygen causes a deshielding of 6.0 ppm in the ^{13}C of $OP(OCH_3)_3$.[5] An even greater deshielding is observed for the methoxy carbon in $[CH_3P(OCH_3)_3]^+$. This same trend is observed in the chemical shift values of the derivatives of $P(CH_3)_3$ reported here and elsewhere.[5] The fact that the ^{13}C in $OP[N(CH_3)_2]_3$ is more shielded than

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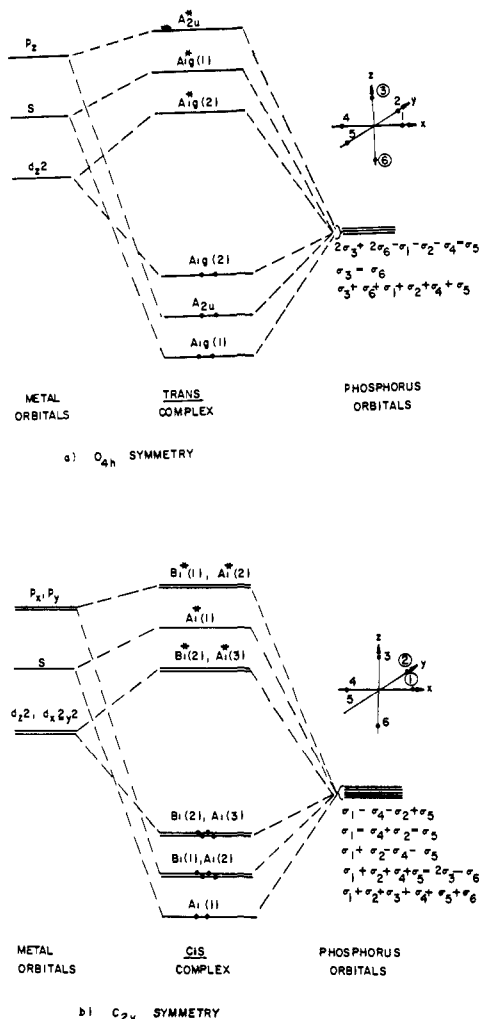
Figure 4. Molecular orbital diagrams of M(CO)₄(PR₃)₂ complexes in the *trans* (a) and *cis* (b) configurations. See text for designations of M and R. Circled positions on the Cartesian coordinate systems represent phosphorus positions while the others denote carbonyl locations.

in P[N(CH₃)₂]₃ appears to be out of line with the observations involving the former ligands.

^{31}P–^{31}P Couplings. The Fermi contact term dominates the coupling mechanism between protons and it is likely that it is of greatest importance for coupling between all atoms.[28–31] Pople and Santry[15] developed a molecular orbital theory which predicts both negative and positive signs for couplings and whose Fermi term is of the form given previously. Although this treatment has been further refined by Pople, *et al.*,[32] the above relationship will suffice here. In the absence of a complete MO treatment of our complicated systems, only a very qualitative discussion of our results can be given at this time.

The sign and magnitude of J_{AB} is determined by the symmetries and energies, respectively, of the dominant electronic transition(s). An excitation from one or-

bital to another of the same symmetry (*i.e.*, sym → sym or antisym → antisym) contributes a negative sign to J_{AB} while a transition involving orbitals of opposite symmetry gives J_{AB} a positive sign. The magnitude of J_{AB} will be influenced by the energy differences between the transitions, the degree of phosphorus 3s-character in the orbitals involved, and the value of the valence s orbital at the phosphorus. Although the magnitude of the s electron density at the nucleus would be expected to increase with substituents of increasing electronegativity, causing an increase in $^2J_{PP}$, it is unlikely that the variation in coupling constants arises solely from this term. It would appear that the dominant effect in determining coupling constants is the summation term in the equation above. Good evidence for this is given by the molecule *cis*-PtCl(CH₃)[P(C₂H₅)₃]₂, which has two platinum–phosphorus coupling constants which differ widely (1719 Hz and 4179 Hz).[33] It is obvious that the $(S_{6sPt}|\delta(r_{Pt})|S_{6sPt})$ term at platinum must be the same for each coupling constant and that the density at each phosphorus will be nearly the same since identical ligands are involved. The large difference in $^1J_{PtP}$ must therefore arise from the differences in the orbitals used in the Pt–P bonds. Moreover, although the s electron densities at the nuclei can affect the magnitudes of coupling constants, they cannot affect the signs. Thus the change in sign for $^2J_{PP}$ for the *trans* chromium complexes shows that in the absence of large excitation energy variations, changes in the coefficients of the s atomic orbitals must be dominating any change in the magnitudes of the s orbital densities at the nuclei.

Without detailed MO calculations on the prohibitively complicated coordination complexes studied here, prediction of the sign and magnitude of $^2J_{PP}$ is not possible. It is worthwhile, however, to consider the possible origins of the signs and the trends of $^2J_{PP}$ in the *trans* and *cis* group VI complexes for which the greatest range of values have been obtained.[34] In Figure 4a is depicted an MO diagram for a *trans* complex in which only the phosphorus orbitals having σ character are considered and in which the ordering of the MO levels is the same as that which is commonly accepted for complexes of O_h symmetry.[35] Because it is not known with certainty how the phosphorus "sp³" lone-pair hybrid compares in energy with the "sp" lone-pair hybrid of the CO group, the three possibilities shown in Figure 5a must be taken into account. We imply nothing quantitative about the energies involved but do assume that the relative ordering of the levels is preserved. As the energy of the phosphorus σ orbital (E_P) changes with respect to that of the CO σ hybrid (E_{CO}), the phosphorus character (orbital coefficient) is altered in the manner shown in Figure 5. Experiment shows that the sign of $^2J_{PP}$ in the *trans* complex is generally positive, which would be consistent with the case

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where $E_P < E_{CO}$ since the transition of lowest energy ($A_{2u} \rightarrow A_{1g}*(2)$) contributes positively to the coupling. Alternatively, the case where $E_P = E_{CO}$ might equally apply if the higher energy transition ($A_{2u} \rightarrow A_{1g}*(2)$) dominates by virtue of the greater phosphorus character in the A_{2u} level. The observation that some *trans* chromium complexes possess negative $^2J_{PP}$ values suggests that E_P approaches or exceeds that of E_{CO} so that the $A_{1g}(2) \rightarrow A_{1g}*(2)$ or $A_{1g}*(1)$ transitions, respectively, can become dominant. As the electronegativity of the phosphorus ligand increases, the sign of $^2J_{PP}$ in the chromium complexes changes from negative to positive. This would be expected on the ground that E_P should drop relative to E_{CO} under these conditions, allowing a transition with a positive contribution to become dominant.

The *cis* complexes (Figures 4b and 5b) constitute a more complicated situation in that the presence of more orbitals affords an increased number of possible transitions. Of the four possible transitions among the $A_1(3)$, $B_1(2)$, $A_1*(3)$, and $B_1*(2)$ levels in the case where $E_P = E_{CO}$, however, the $B_1(2) \rightarrow B_1*(2)$ excitation is expected to dominate both of the positively contributing transitions because of the smaller orbital coefficients associated with the latter. The experimental range of $^2J_{PP}$ values for this configuration is -12.4 to -78 Hz. The present upper limit is not far from zero and it might be possible to approach zero coupling even more closely with more electropositive phosphorus ligands, that is, when $E_P > E_{CO}$. From the diagrams in Figure 5b, an upper limit of zero would be predicted due to cancellation ($E_P > E_{CO}$) and there would be no likelihood of encountering sign changes in *cis* complexes with electropositive phosphorus ligands. Although a return to zero coupling would also be predicted if E_P becomes appreciably less than E_{CO}, this may be precluded from occurring if in all of these complexes E_P remains approximately equal to or larger than E_{CO}. In both the *cis* and the *trans* complexes a numerical rise in $^2J_{PP}$ is seen as the electronegativity of the phosphorus ligand increases. This is consistent with the expected increase in the phosphorus s orbital coefficients and the valence s orbital density value at the nucleus.[36]

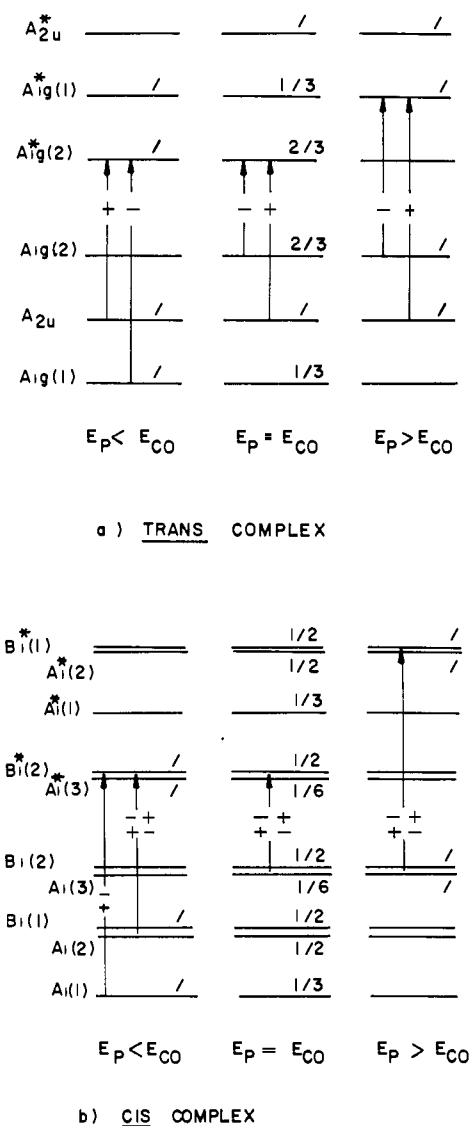**Acknowledgments.** The authors acknowledge support of this work by the National Science Foundation

Figure 5. Molecular orbital level arrangements and fractional phosphorus character in appropriate orbitals for $M(CO)_4(PR_3)_2$ complexes in the *trans* (a) and *cis* (b) configurations. See text for designations of M and R. Three conditions of E_P with respect to E_{CO} are shown for each case. Signs refer to the contributions of the transitions to the overall sign of $^2J_{PP}$.